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(54) Title: THERMOPLASTIC FLUORO RESIN COMPOSITIONS AND MOULDED AND/OR EXTRUDED ARTICLES PRODUCED THEREFROM		
(57) Abstract The present invention provides a thermoplastic fluoro resin composition improved in mouldability at high speed and adhesive and antistatic properties which makes it possible to produce moulded and/or extruded articles. The thermoplastic fluoro resin composition comprises (A) thermoplastic fluoro resin(s) containing at least 50 % by weight of vinylidene fluoride and (B) polyoxyalkylene and/or polyether ester, the weight ratio of (A)/(B) being 99.5/0.5 to 55/45. The moulded and/or extruded articles obtained therefrom have the same improved properties indicated above.		

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SPECIFICATION**THERMOPLASTIC FLUORO RESIN COMPOSITIONS AND MOULDED
AND/OR EXTRUDED ARTICLES PRODUCED THEREFROM****TECHNICAL FIELD**

5 This invention relates to thermoplastic fluoro resin compositions and moulded articles produced therefrom. The thermoplastic fluoro resin compositions of the present invention have improved mouldability, flexibility, adhesive and antistatic properties and can be used to produce moulded articles, films and fibres.

10 PRIOR ART

Thermoplastic fluoro resins possessing high weather- and chemical resistance are utilized in many fields such as paint, electrical or electronics components, steel pipe liner, materials for chemical plant and stain- and weather-resistant film. These resins, however, are difficult to combine with
15 other materials owing to their poor adhesiveness. Fluoro resins are resistant to staining but show rather poor antistatic properties. Fibres and films based on fluoro resin are difficult to stretch owing to their high viscosity and crystallinity. The use of a polymer possessing a low degree of polymerization to permit high-speed moulding results in loss of strength of the moulded articles.

20 In order to solve these problems, combinations with other polymers have been proposed such as with polymethyl methacrylate resin (PMMA) (JP-A-60-110912), isobutylene copolymer (JP-A-54-106622), acrylate resin (JP-B-56-20610), blend with other fluoro resins (JP-B-4-44012, JP-A-60-104514), the addition of a plasticizer (JP-A-55-84413), polyolefin (JP-A-62-268811),
25 inorganic soap (JP-A-61-174418), fluorocarbon wax (JP-A-60-115652) and their combination (JP-A-6-101114). Spinning and drawing techniques are also known (JP-A-53-22574). The results are not satisfactory.

DISCLOSURE OF THE INVENTION

30 An objective of the present invention is to improve the flexibility, adhesive properties and antistatic properties of thermoplastic fluoro resin compositions.

The present invention provides a thermoplastic fluoro resin composition comprising (A) 99.5 to 55 % by weight of thermoplastic fluoro resin(s) containing at least 50 % by weight of vinylidene fluoride and (B) 0.5 to 45 parts
35 by weight of polyoxyalkylene(s) and/or polyether ester resin(s).

"The thermoplastic fluoro resin (A)" contains at least 50 % by weight of vinylidene fluoride (VF2), and may contain less than 50 % by weight of other components.

The comonomers may be tetrafluoroethylene (TFE), trifluoroethylene, chlorotrifluoroethylene (CTFE), vinyl fluoride (VF), hexafluoropropylene (HFP), ethylene and/or perfluoroalkyl vinyl ethers.

As mentioned above, the content of VF2 in resin (A) is at least 50 % by weight, preferably above 70 % by weight, more preferably above 90 % by weight. Resin (A) according to the present invention can be obtained by any usual polymerization method including emulsion polymerization and dispersion polymerization and preferably has a melt flow index (MFI) measured at 230 °C under a load of 2.16 kg according to ISO 1133 in the range of 0.1 to 500 g/10 min.

"The polyoxyalkylene (B)" is a polymer of oxyalkylene. Generally, a polyoxyalkylene can be prepared by ring-opening polycondensation of an alkylene glycol with an alkylene oxide of relatively low molecular mass and by ring-opening polymerization of an alkylene oxide of relatively high molecular mass. The polyoxyalkylene (B) may be poly(oxyethylene), poly(1,2- or 1,3-propylene)oxide, polytetramethylene oxide, polyhexamethylene oxide, a block, random or graft copolymer of ethylene oxide and propylene oxide and a block or random copolymer of ethylene oxide and tetrahydrofuran. Polyoxyethylene is preferred.

The number-average molecular weight \overline{M}_n of the polyoxyalkylene is 1,000 to 5,000,000, preferably 10,000 to 1,000,000, and more preferably 20,000 to 600,000 and depends on applications. For example, a relatively low molecular mass (10,000 to 50,000) is used for applications in which antistatic properties and stain resistance are required, while relatively a high molecular mass (100,000 to 1,000,000) is used when longer life of these properties and mouldability are required. Too high molecular masses (over 5,000,000) are not preferred because of too high viscosity and low thermal stability.

"The polyether ester resin (B)" according to the present invention is a resin in which polyoxyalkylene units of relatively low molecular mass such as defined above are bonded to each other by ester bonds through a compound of relatively low molecular mass, called a "bonding compound". Consequently, the polyether ester resin (B) according to the present invention is different from a polyetherpolyester block copolymer (so-called thermoplastic polyester elastomer, TPEE).

The number-average molecular weight \overline{M}_n of the polyoxyalkylene units is generally lower than 20,000, preferably lower than 10,000, more preferably lower than 5,000.

The polyoxyalkylene units are bonded to each other through a compound of relatively low molecular mass to produce a polyether ester having a molecular mass higher than 40,000, preferably being 100,000 to 1,000,000. As indicated above, a polyoxyalkylene of high molecular mass is difficult to mix with thermoplastic fluoro resin owing to high crystallinity, so that the resulting product shows poor uniformity and antistatic properties when compared with a polyether ester obtained by bonding polyoxyalkylene units through relatively low molecular mass compounds.

The relatively low molecular mass bonding compounds have generally a molecular mass of less than 500 and may be chosen from carboxylic acids, hydroxyl compounds, epoxy compounds and oxazoline compounds (in this case, there are some amide bonds but the polyoxyalkylene units must be bonded by ester bond). The choice of preferred bonding compounds depends on the terminal groups of the polyoxyalkylene units. For example, if the polyoxyalkylene units have hydroxyl end groups, dicarboxylic acids, bisoxazoline compounds or the like are preferably used. If the polyoxyalkylene units have carboxyl end groups, dihydroxyl compounds, diepoxy compounds, bisoxazoline compounds or the like are preferably used.

As bonding compounds of low molecular mass, the carboxylic acids may be oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, isophthalic acid, terephthalic acid, trimellitic acid, trimesic acid and pyromellitic acid. The hydroxy acids may be glycolic acid and hydroxybenzoic acid. The hydroxyl compounds may be ethylene glycol, trimethylene glycol, tetramethylene glycol, pentamethylene glycol, neopentyl glycol, hexamethylene glycol, glycerol and trimethylolpropane. The oxazoline compounds may be ethylene bisoxazoline and phenylene bisoxazoline. The epoxy compounds may be bisglycidyl terephthalate or the like.

Among them, the polyether ester obtained from polyoxyalkylene units with hydroxyl end groups and a dicarboxylic acid or its derivative is easy to produce and hence is advantageous. Derivatives of dicarboxylic acids may be used such as anhydrides and C₁-C₃ alkyl esters.

The weight ratio (A/B) of thermoplastic fluoro resin(s) (A) to polyoxyalkylene(s) and/or polyether ester(s) (B) is 95.5/0.5 to 55/45, preferably 95/1 to 70/30, and depends on the application.

The composition according to the present invention can be used directly from a dry blend of components (A) and (B) but is preferably melt-kneaded before moulding. The kneading can be done by any known technique without

using any compatibility-improving agent in any known kneader such as a Banbury mixer, rubber rolls and a single- or a twin-screw extruder. The resin composition is melt-kneaded usually at 100 to 300 °C, preferably 150 to 270 C, to prepare a moulding compound. The mouldability of the composition according to the present invention in injection and extrusion moulding is excellent because no rise in pressure caused by viscosity is observed even in high-speed moulding.

The composition according to the present invention can be spun by the usual melt-spinning drawing techniques to produce fibres and can be extruded to produce films, sheets and plates. The fibre can be multifilament, monofilament, staple, or be made into a textile or knitted article or nonwoven web and can have a solid, hollow or profiled cross section. The fibre can be mixed advantageously with other materials to produce a mixed nonwoven web because of its improved adhesive properties.

The composition according to the present invention may contain known additives such as antioxidants, antipyrrolysis agents, UV absorbers, antihydrolysis agents, colorants (dyes, pigments), antistatic agents, electrically conductive agents, crystal nucleating agents, plasticizers, slip agents, lubricants, mould release agents, flame retardants, reinforcements, fillers, adhesives and tackifiers.

The compositions according to the present invention possess useful properties such as mouldability, flexibility and antistatic and adhesive properties and are useful as materials for moulded materials, fibre and film.

The composition according to the present invention shows a reduced pressure increase in high-speed moulding and the moulded articles obtained therefrom show improved flexibility, antistatic properties and adhesion to other materials and possess improved properties for moulded articles, fibres and films.

During the preparation of the resin composition according to the present invention, the pressure is not greatly increased, even in high-speed moulding operation.

WAYS OF CARRYING OUT THE INVENTION

The following test methods were used in the following Examples :

- 1) Melt Flow Index (MFI) of fluoro resin
determined at 230 °C under a load of 2.16 kg according to ISO 1133 and expressed in terms of g/10 min.
- 2) Viscosity-average molecular mass of polyoxyalkylene (POA) and polyether ester (PEE)

calculated by Bailey's experimental equation from the solution viscosity of an aqueous solution containing 0.1 % by weight of polymer at 35 °C

3) Preparation of compositions

a) Pellets of fluoro resin and of POA are mixed in a blender and extruded using a single-screw extruder (20 mm \varnothing) equipped with a die of 3 mm \varnothing to prepare pellets for fibre and film at barrel temperatures of 160 to 260 °C and at a screw speed of 10 rev/min.

b) Predetermined amounts of pellets of fluoro resin and of PEE are blended in a blender. The resulting mixture is extruded using a single-screw extruder having a barrel temperature of 160 to 260 °C at a screw speed of 20 rev/min through a die having a hole of 3 mm \varnothing to prepare pellets from which samples of fibre, film and moulded articles are prepared.

4) Mouldability at high speed

evaluated as the increase in head pressure when the screw speed was raised from 10 rev/min to 20 rev/min.

5) Flexural modulus

according to ISO 178.

6) Impact strength

according to ISO 180/1A.

7) Antistatic properties

A film of 1 mm thickness was prepared from the pellets prepared in 3a) or in 3b) and its surface resistivity was measured at 23 °C in 50 % relative humidity according to JIS K -6911.

The following polymers were used in the Examples :

PVDF-1: 100 % PVDF homopolymer , MFI = 20

PVDF-2: copolymer of VF2 and HFP (15%), MFI = 10

PVDF-3: copolymer of VF2 and HFP (5%), MFI = 8

POA-1: polyoxyethylene (viscosity-average molecular mass of 150,000)

POA-2: polyoxyethylene (viscosity-average molecular mass of 280,000)

POA-3: polyoxyethylene (viscosity-average molecular mass of viscosity-average molecular mass of 20,000)

POA-4: polyoxyethylene (viscosity-average molecular mass of 10,000)

PEE-1 polyether ester (viscosity-average molecular mass of 150,000) prepared by polycondensation of polyoxyethylene possessing a viscosity-average molecular mass of 2,500 and dimethyl terephthalate.

PEE-2 polyether ester (viscosity-average molecular weight of 130,000) prepared by polycondensation of polyoxyethylene of viscosity-average molecular mass of 5,000 and adipic acid.

Example 1

5 Pellets of PVDF-1 and pellets of POA-1 were blended in a weight ratio of 70/30 and fed into a single-screw extruder set at a temperature of 250 °C to produce pellets at a head pressure of 5 MPa. The increase in head pressure was only 1.4-fold when the screw speed was doubled.

10 A test sample prepared by an injection moulding machine from the pellets at a mould clamping pressure of 80 tons showed a flexural modulus of 1,100 MPa, an impact strength of 11 kJ/m² and a surface resistivity of 10¹⁰ Ω/L².

Example 2

15 Example 1 was repeated but the pellets of PVDF-1 and pellets of POA-1 were blended in a weight ratio of 95/5 at a head pressure of 5 MPa. The head pressure was increased 1.5-fold, the flexural modulus was 1,150 MPa, the impact strength 10 kJ/m² and the surface resistivity 10¹¹ Ω/L².

Comparative Example 1

Example 1 was repeated but only PVDF-1 was used.

20 In this case, the head pressure was 8 MPa, the increase in head pressure was 1.8-fold, the flexural modulus was 1,800 MPa, the impact strength was 5 kJ/m² and the surface resistivity was 10¹⁴ Ω/L².

25 When compared with Examples 1 and 2, this result reveals that the composition containing polyoxyalkylene improves mouldability at higher speed, flexibility and the antistatic properties.

Examples 3 to 6

30 The POA-1 of Example 1 was replaced by POA-2 (Example 3), POA-3 (Example 4) and POA-4 (Example 5) and the PVDF-1 of Example 1 was replaced by PVDF-2 (Example 6, in this case the barrel temperature was set at 240 °C).

These samples also showed improved mouldability at higher speed and antistatic properties (the increase of head pressure was 1.5, 1.4, 1.3 and respectively 1.3-fold when the screw speed was doubled and the surface resistivity was 10¹⁰ Ω/L² in Examples 3, 4 and 6 and 10¹¹ Ω/L² in Example 5).

Example 7

35 A filament was spun at 270 °C through a die having a hole of 0.3 mm ø using the pellets of Example 1.

The observation of the resulting fibre by microscope showed a structure of a fine dispersion although not perfectly compatible. The fibre has good adhesion to polypropylene fibre. The fibre made of PVDF-1 alone (Comparative Example 1) has no adhesion to polypropylene.

Example 8

PVDF-1 and PEE-1 were mixed in a weight ratio of (A/B) = 75/25. The resulting mixture was extruded using a single-screw extruder (barrel temperature = 250 °C) to obtain strands from which pellets were prepared. The head pressure at extrusion was 4.5 MPa. This extrusion head pressure increased to 1.3-fold when the number of revolutions of the screw was doubled.

The moulded test samples prepared from the pellets with an injection moulding machine (clamping pressure = 80 tons) showed a flexural modulus of 1,100 MPa, an impact strength of 10 kJ/m² and the surface resistivity was 10¹¹ Ω/L².

Example 9

Example 8 was repeated but POA-1 was used instead of PEE-1.

The extrusion head pressure was 5 MPa, which is 10 % higher than in the case of PEE-1. A sheet of 1 mm thickness prepared from this composition showed a surface resistivity of 5.10¹⁰ Ω/L² so that this film was a little less antistatic than the one of PEE-1.

Example 10

Example 8 was repeated but the A/B ratio was changed to 95/5.

The extrusion head pressure was 5 MPa. The increase in pressure was 1.4-fold, the flexural modulus was 1,150 MPa, the impact strength was 9.5 kJ/m² and the surface resistivity 8.10¹⁰ Ω/L².

Comparative Example 3

Example 8 was repeated but PVDF alone was used.

The extrusion head pressure was 8 MPa. The increase in pressure was 1.8-fold, the flexural modulus was 1,800 MPa, the impact strength was 5 kg J/m² and the surface resistivity 10¹⁴ Ω/L².

In comparison with the results of Examples 1 and 2, it appears that high-speed mouldability, flexibility and antistatic properties were improved by adding the polyether ester resin.

Example 11

Example 8 was repeated but the PVDF-1 was replaced by PVDF-3 and PEE-1 was replaced by PEE-2.

CLAIMS

1. Thermoplastic fluoro resin composition comprising (A) 99.5 to 55 % by weight of thermoplastic fluoro resin(s) containing at least 50 % by weight of vinylidene fluoride and (B) 0.5 to 45 parts by weight of polyoxyalkylene(s) and/or polyether ester(s).
5
2. Composition according to claim 1, wherein the polyoxyalkylene is polyoxyethylene.
3. Composition according to claim 1 or 2, wherein the polyether ester is obtained from polyoxyalkylene units with hydroxyl end groups and a dicarboxylic acid or its derivative.
10
4. Composition according to claim 1 to 3, wherein the weight ratio of (A/B) is 99/1 to 70/30.
5. Moulded articles made of and/or based on and/or comprising a composition as defined in any one of claims 1 to 4.
- 15 6. Extruded articles made of and/or based on and/or comprising a composition as defined in any one of claims 1 to 4, in the form of fibre, film, plate or sheet.